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Metallic Calcium

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METALLIC CALCIUM

AND ITS APPLICATION TO IRON FOUNDING

BY

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THESIS

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METALLIC CALCIUM

and

ITS APPLICATION TO IRON FOUNDING.

Until within the last few years little attention has been given by chemists and inventors to the subject of metallic calcium. Yet as early as 1808, Davy had succeeded in isolating the pure metal in sufficient quantities to study its characteristics and properties. It is described in general chemestries as a bras-yellow, lustrous metal, which is contact with moist air becomes coated with an hydroxide and carbonate coating, and that at ordinary temperatures it would decompose water like Potassium or Sodium.

Bunsen and Matthiessen, the German Chemists took up the work of obtaining this metal later, (about 1854), and the incomplete information that they gave science on the electrolytic reduction of calcium salts, was the only information available until very recent times, when the electrolytic decomposition of calcium chloride has been very carefully and thoroughly investigated by Dr. W. Eorschers and his associates.

These last named men have been very successful and have succeeded in electrolytically reducing metallic calcium from its chloride in quantities, and at a surprisingly moderate expense.

And now that it has been practically demonstrated that metallic calcium can be produced in quantities and at a low cost, there comes the question of its application. There are many possibilities in this field, and some of them no doubt are of great

practical value. Time conpled with intelligent experimenting may yet develope these possibilities beyond all expectation.

One of the possibilities of the future application of metallic calcium might be as a fixer of nitrogen from the air, thus giving a new source for nitrogen bearing compounds. Calcium has an affinity for nitrogen such, that if brought in contact with the pure gas, it should be made to combine chemically with it, under proper conditions, thus giving a nitride or related compound of nitrogen and calcium. The world's supply of nitrogen compounds is derived at present almost entirely from the Nitre beds of Chili. In course of time these beds will become exhausted, and the practical world as well as the scientific be brought to consider some such new proposition. Calcium offers a rational possibility for the solution of the problem.

The possibility of the application of metallic calcium to irons is the one investigated in this thesis. The idea being that metallic calcium, having a very high chemical affinity for sulphur and phosphorous, would, if introduced into molten iron, combine with these injourous elements forming phosphides or sulphides, or also unite with oxygen, almost always found in some form in molten iron, to form phosphates, sulphites, sulphates, or related compounds of calcium, which would rise to the surface and be removed by skimming or some method of pouring as by siphon ladle thus removing the impurities.

The calcium itself being so readily oxidized, and somewhat difficult to obtain pure, it was thought best to utilize some other metal or substance to alloy with it, and act as a carrier. For the purpose in view nothing seems more suited to the purpose than

Aluminium. Aluminium alloys readily with metallic calcium and is itself beneficial to iron, if added within certain limited quantities, absorbing gases in molten cast iron so that the castings are of uniform structure and free from blow holes. It also gives molten iron great fluidity, so that good sharply outlined castings result, and it has been proven beyond doubt by Keep and others, that within certain limits, the addition of Al increases the strength of the castings, and lastly that it is instrumental in causing increased separation of the carbon of the iron in form of graphite, thus producing a softer, more easily machined product.

From the results obtained in this thesis investigation it would appear that the assumptions made in the beginning were to a reasonable extent at least correct. The electrolytic reduction of the calcium from its chloride was accomplished with some difficulty, as the latter work of Borscher and his associates had not yet been made public and the author of this work was compelled to plunge somewhat blindly on this part of the work. The desired alloy was obtained too late to make a thorough investigation of its effects when applied to irons. The method of proceedure was as follows.

The first attempt at electrolytic decomposition of $CaCl_2$ in presence of metallic aluminium was conducted as follows: The cell consisted of a large French clay pipe, through the stem of which, was inserted and cemented in a copper wire convected with the negative pole of a direct current dynamo. This wire extended well up into the bowl of the pipe so as to come within contact with fused aluminium which filled the bottom part of the bowl. Above this fused aluminium the bowl was filled to two-thirds full of fused calcium chloride into which dipped a carbon electrode connected to the other,

the positive pole of the dynamo. The contents of the pipe were kept fused by means of a small blast lamp burning illuminating gas and draft forced by compressed air. It will be seen that the above furnished a complete electrolytic cell. The fused $CaCl_2$ forming the electrolyte, the carbon electrode the anode pole, and the fused mass the aluminium, the cathode pole.

After the blast had been heating the pipe sufficiently long to thoroughly fuse the contents, the current was switched on from the dynamo. In this particular case, the current had a volume of seven ampheres at 10 volts and was allowed to pass through the electrolyte for about 10 minutes, the cell being heated meanwhile by the blast lamp. While the current was passing through the cell the electrolyte was in constant agitation, chlorine fumes escaped from the region of the carbon electrode while there was a regular intermittent display of small flames all over the surface of the fused chloride of calcium. This was evidently burning metallic calcium particles, which liberated below, found their way to the surface and there took fire.

After the action had lasted about 10 minutes, the current was turned off, the pipe cooled, allowing the contents to harden, and then broken open. In the bottom was found a button with the general appearance of metallic aluminium, but having perhaps more of a gray tinge than ordinary bright aluminium. This button was thoroughly boiled and washed in water in order to free from any adhering $CaCl_2$, and a few filings dissolved in HCl and tested as follows for Ca. First the Al was precipitated and separated together with any Fe present as the hydroxide, NH_4OH being reagent used. The filtrate from this precipitation was then treated with $(NH_4)_2C_2O_4$, and a white precipitate of CaC_2O_4 was immediately in evidence,

showing presence of Ca in Al button. A careful quantitative analysis
of the remainder of button was then made, the Ca being precipitated as
before $\overset{\text{as}}{\wedge}$ CaC_2O_4 after removing Al and Fe as hydroxides. The CaC_2O_4
was collected on filter paper and thoroughly washed to free from all
$(NH_4)_2C_2O_4$, and then dissolved in sulphuric acid, oxalic acid and
calcium sulphate resulting as represented by the equation

$$CaC_2O_4 + H_2SO_4 = CaSO_4 + H_2C_2O_4.$$

This solution of oxalic acid was then carefully titrated (hot)
against a standard solution of $KMnO_4$ which had been previously
standardized against an accurately weighed amount of $H_2C_2O_4 \cdot 2H_2O$.
The data of this analysis is given below.

CUT OF APPARATUS.
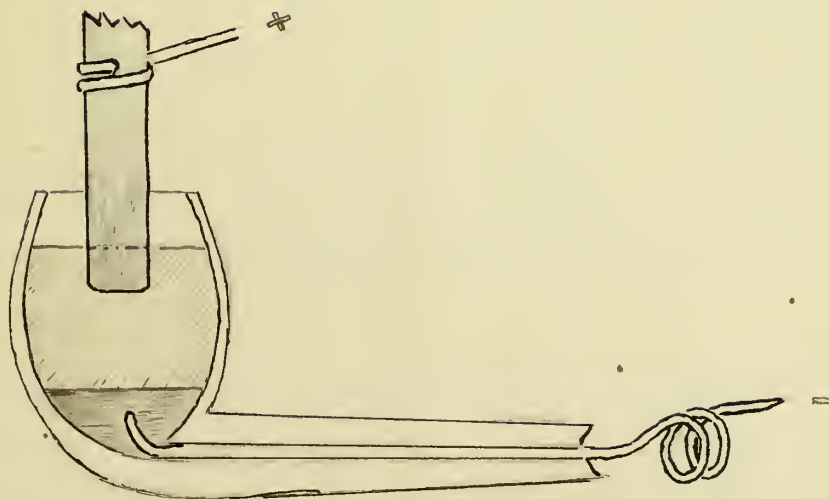
ANALYSIS Ca·Al ALLOY (pipe cell).

1. Standardization of $KMnO_4$ sol. (about 3 grams $KMnO_4$ in 1 1.)

Weight oxalic acid = .2507 grams.

required 51 cc. $KMnO_4$ sol.

1 cc. $KMnO_4$ = 0.004916 grams $C_2H_2O_4 \cdot 2H_2O$.

or from proportion $C_2H_2O_4 \cdot 2H_2O : Ca :: Wt. \, C_2H_2O_4 \cdot 2H_2O$.

126 : 40 :: .004916 : x = .00156

1 cc. $KMnO_4$ = 0.00156 grams Ca

2. Wt. Ca·Al Alloy = 3.4945 grams.

Took aliquote parts of sol.

1st 1/5 required 24.2 cc. S. $KMnO_4$ sol.

2nd 1/5 " 24.2 cc. S. $KMnO_4$ sol.

5 x 24.2 = 121.0 cc. $KMnO_4$ for entire sample.

121.0 x 0.00156 = 0.18876 grams Ca in sample.

0.18876 ÷ 3.4945 x 100 = 5.40% Ca in sample.

xx The quantity of alloy obtained by means of the pipe cell was too small to enable it to be tried on irons, but the experiment did prove several things which were previously in doubt as follows:

1. Metallic Ca can be readily obtained by electrolysis of fused $CaCl_2$.

2. That the Ca liberated as per above will alloy it brought in contact with fused Al.

3. That considerable Ca is wasted, either going into solution again under certain conditions of temperature as $CaCl_2$ or CaCl, or rising to the surface to be oxidized by the air.

4. An electric current of comparitively small volume and potential will effect the electrolysis of the $CaCl_2$.

(3) Is calculated as follows, from Faraday's law we have "the amounts of products resulting from decomposition by electrolysis are proportioned to their atomic weights", and by experiment recognized by Act of Congress.

1 A current deposits 0.001118 grams Ag per sec. from $AgNO_3$ sol.

1 A   "   "   0.06708   "   " " min. "   "   "

ro :: o Ca to Ag = $\frac{107}{40}$. hence

   1 A   = 0.06708 ÷ 2.6 = 0.0258 grams Ca per min.

   1 A   = 1.548 grams Ca per hr.

   15 A   = 23.220 "   "   "   "

   7 A   = 10.836 "   "   "   " = 1.806 g. Ca per 10 min.

Actual yield @ 7A = 0.191 grams Ca per 10 min.

   ∴ efficiency of cell = about 10%.

in order to obtain an alloy of higher Ca content and in greater quantities, various new cells were tried and currents of increased volume were employed in all attempts after the trial with pipe cell. Graphite cells proved a failure owing to good conducting property of cell walls. Many attempts were also made to utilize the fused Al as the cathode of the larger cells but all proved very inefficient and it was not until the following cell was devised that sufficient amounts of high content Ca alloy could be obtained to warrant a trial of the alloy on molten cast iron, in oder to determine the effect of metallic calcium on the S and P contained in the iron.

       This cell was devised to fulfil as nearly as possible the following conditions.

   1. Cell itself to be non conducting (used fire-clay assay
       crucible).

2. Concentration of current to be obtained by running current into cell through iron points piercing cell through the sides, these points forming cathode pole.

3. The upper surface of fused Al rising just below cathode points. The Al not forming cathode pole as formerly.

4. Regulation of heat distribution so as to get a maximium amount of heat at cathode points, and minimum amount of heat above what is necessary to fuse $CaCl_2$ in electrolyte.

   The cell finally decided upon as best fulfiling these points was a fire clay crucible suspended in a circular blast furnace by means of a circular wrought iron plate as shown in drawing below. This plate kept the flame of the blast confined to lower part of cell, keeping the aluminium and iron cathode points very hot, while the upper part of electrolyte was barely kept fused. A crust forming on top of fused $CaCl_2$ protecting the Ca particles in same from coming in contact with the air and oxidizing until the circulation in electrolyte might carry them down again to alloy with the fused aluminium in bottom of cell.
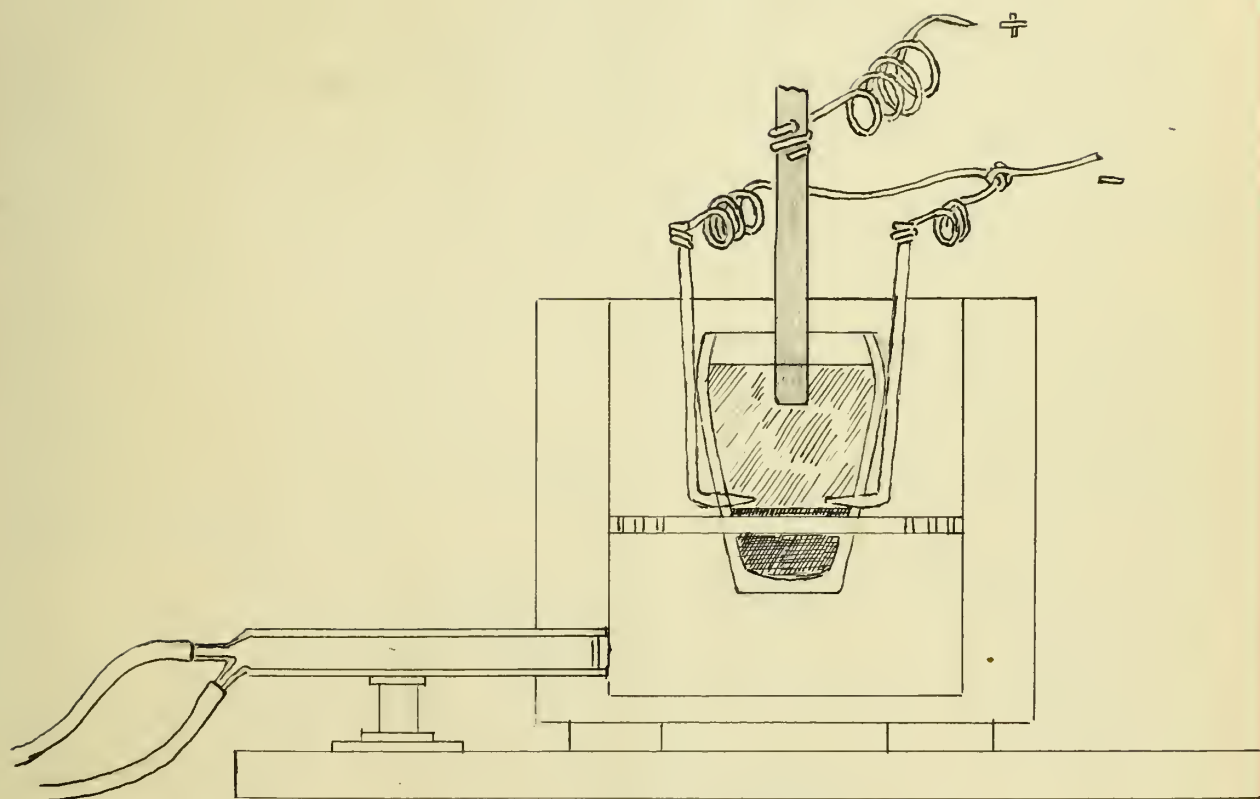
The current was carried into the furnace to cathode points by 1/4" wrought iron bars the ends of which formed the cathode points. In two last runs made with this type of cell, a current of from 20 to 30 ampheres was used. This current was obtained by charging a storage battery of 36 (thirty six) cells with the dynamo and then using current from storage battery to effect electrolytic decomposition in cell. From 50 to 75 grams Al were used and the 23 A current run through the fused electrolyte for about 1/2 hour after which time the battery became exhausted and the 10 A current direct from dynamo would be used as long as desired, in last two cases mentioned, the 10 A current was used for but 10 to 15 minutes before iron cathode points were decomposed or burned away, when of course the process had to be discontinued. An analysis of the Ca·Al alloy formed from the last two runs showed a percentage of Ca of 12.51% and 14.57% respectively.

<div align="center">CHEMICAL ANALYSIS OF Ca·Al alloy. 4/17 .03.</div>

<div align="center">STANDARDIZATION OF $KMnO_4$ sol.</div>

Wt. $H_2C_2O_4 \cdot 2H_2O$ = 0.3625.

    required   74.2 cc. $KMnO_4$.

        1 cc. $KMnO_4$ = 0.0488 grams $C_2H_2O_4 \cdot 2H_2O$.

        1 " " = 0.00154 " calcium.

1.   Wt. alloy   = 0.7867.

    No. cc. $KMnO_4$ = 75.1

    Wt. Ca   = 75.1 x .00154 = .1156 grams.

    Per cent Ca   = 14.57

2.   Wt. alloy   = 0.6582

    No. cc. $KMnO_4$ = 53.5

    Wt. Ca   = 53.5 x 0.00154 = .0824.

    Per cent Ca   = 12.51

In order to determine the effect of the metallic calcium in above alloys on sulphur and phosphorous in cast irons the following test was made.

To a ladle containing 25# molten cast iron just run from cupalo, was added a piece of the alloy weighing 43 grams of 14.57% Ca and one of 68 grams weight containing 12.51% Ca making in all a weight of 111 grams alloy to about 11,250. grams iron. The whole mass was then well mixed and stirred and cast into small test bars. On adding this alloy to the molten cast iron the iron immediately began to boil and its surface covered with brilliant display of colors. The surface was well skimmed before pouring. A blank of pure iron poured at same time was also cast in small test bars.

The action expected was that the metallic calcium carried by the aluminium would combine chemically with the P and S, and perhaps O inclosed in iron, to form calcium phosphides or phosphates and calcium sulphides or sulphates which would separate out from the iron solution and be removed as a scum or film on skimming or be removed by volatilization. A chemical analysis of treated and non treated samples of iron would go to show that in case of treated samples a considerable part of both P and S were removed.

CHEMICAL ANALYSIS.

BLANK AND TREATED CAST IRONS.

STANDARDIZATION $KMnO_4$ sol.

Wt. 99.7% S·Fe wire   = 0.1187

" pure " " "   = 0.1183

Required 22.6 cc. A. $KMnO_4$.

1.   1 cc. $KMnO_4$ = 0.0056 gr. Fe.

1 cc. "   = 0.00008659 g. Phos.

Wt. 99.7% S·Fe wire   =   0.1112

" pure " " "   =   0.1108

  Required 20.00 cc. S.KMnO$_4$.

      1 cc. KMnO$_4$ =   0.00554

      1 cc.   "   =   0.00008659 Phos.

              DETERMINATION OF PHOSPHOROUS.

Wt. treated sample ÷ w. t   =   5.2210

"   "   = 3.2193

                                          2.0012

   diluted to 500 cc. took 25 cc. (1/20) aliquote parts.

   1. Required 6.7 cc. KMnO$_4$ 2 required 6.7

       Blank   .2   Blank   .2

               6.5   6.5

   3.6.8

       2
              6.5 × 20 = 130 × 0.00008695 = 0.011309 P.
   6.6 cc.
              0.01130 ÷ 2.0012 × 100 = 0.564% P.

              DETERMINATION OF PHOSPHOROUS (con.).

Non-treated iron

Wt. Sample ÷ w.t   =   5.2195

"   "   = 3.2193

"   "   =   1.9997

   diluted to 500 cc. took 25 cc. (1/20) aliquote pts.

       1. Required 10 cc. KMnO$_4$ sol. 2.   9.9 cc.
           Blank   .2 cc. "   "   .2 cc.
                   9.8 cc.   9.7 cc.

   9.8 × 20 × .00008695 ÷ 1.997 × 100 = 0.851% P.

   Non-treated iron

Wt. sample w.t   =   5.2193

"   "   =   <u>3.2198</u>

"   "   =   1.9995

      Required   9.9   9.6 $KMnO_4$

                  <u>.2</u>   <u>.2</u>   Blank

               9.7   9.4

9.5 x 20 x .00008695 ÷ 1.9995 x 100 = 0.826% P.

DETERMINATION OF SULPHUR.

Treated iron.

Wt. sample + w.t No. 1   =   8.8213

"   "   =   <u>3.8035</u>

                               5.0178

    1 cc. Standard Iodine sol.   =   0.0045 grams S.

    Required   5.8 cc. S. Iodine.

5.8 x .0045 = .00261 ÷ 5.0178 x 100 = 0.052% S.

DETERMINATION OF S. (CON.).

Treated cupalo iron No. 2.

Wt.   sample + w.t   = 8.8218

"   "   = <u>3.8035</u>

                           5.0183

    Required 5.6 I. Sol.

5.6 x 0.0045 = .00252 ÷ 5.0183   =   .050% S.

Non treated iron No. 3.

Wt.   sample + w.t   =   8.8031

"   "   =   <u>3.8035</u>

Non-treated.   4.9996

    Required 6.6 cc. S. I. Sol.

6.6 x .0045 ÷ 4.9996 x 100   = 0.06% S.

Non-treated.

Wt. sample + w.t No. 4 (Non. T)   = 8.8078

   "   "   = <u>3.8035</u>

                                    5.0043

Required 7.0 cc. I. Sol.

$7 \times 0.0045 + 5.0043 \times 100$ = .062% S.

SUMMATIONS.

Blank sample   = 0.826% P.

Treated (CaAl alloy) = 0.564% "

Decrease   = 19.51% total P.

Blank sample   = 0.062% S.

Treated (CaAl alloy) = 0.050% "

Decrease   = 19.35% total P.

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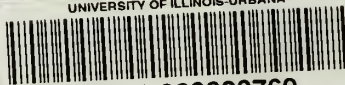
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